

NANO COMMENTARY

Open Access

Magnetic $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires at room temperature using Cu dopant and annealing

Youn Ho Park¹, Ryong Ha¹, Tea-Eon Park², Sung Wook Kim¹, Dongjea Seo¹ and Heon-Jin Choi^{1*}

Abstract

Single-crystal, Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires were grown on GaN/ Al_2O_3 substrates via a vapor-liquid-solid (VLS) mechanism using Ni/Au bi-catalysts. The typical diameter of the $\text{Cu}:\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires was 80 to 150 nm, with a typical length of hundreds of micrometers. The as-grown nanowires exhibited diamagnetism. After annealing, the nanowires exhibited ferromagnetism with saturation magnetic moments higher than $0.8 \mu_B$ ($1 \mu_B \times 10^{-24} \text{ Am}^2$) per Cu atom at room temperature by the measurements using a superconducting quantum interference device (SQUID) magnetometer. X-ray absorption and X-ray magnetic circular dichroism spectra at Cu $L_{2,3}$ -edges indicated that the doped Cu had a local magnetic moment and that its electronic configuration was mainly $3d^9$. It possessed a small trivalent component, and thus, the n-type behavior of electrical property is measured at room temperature.

Keywords: InGaN; Nanowires; Diluted magnetic semiconductors (DMS); Copper dopant; Annealing

Background

In addition to manipulating the charges of electrons, spintronic devices also control the spins of electrons. This innovative technique promises to be one of the next-generation concepts that will lead to the replacement of conventional devices. Recently, not only bulks but also one- and two-dimensional channels are considered as candidates for developing spintronic devices [1-3]. Several III-V compound nanowires exhibit characteristic advantages for this application. Both of the strong spin-orbit interactions induced from inversion asymmetry in wurtzite or zinc blende structure and one-dimensional structures have a potential of high efficiency for spin transport.

To develop spintronic devices, ferromagnetic materials must be used as an electrode. The main principle underlying the operation of spintronic devices is that the spin-polarized current is injected from a ferromagnetic electrode to the semiconductor channel and detected by placing a ferromagnetic detector on the other side of the channel. However, due to the lattice mismatch between the ferromagnet and the semiconductor, the spin injection efficiency is insufficient. Semiconductors doped with a transition metal, the so-called diluted magnetic semiconductors

(DMSs), are promising candidates for resolving this problem. According to the principle of mean field theory [4], transition metals such as Sc, Ti, V, Cr, Mn, Fe, Co, and Ni that have partially filled d states can be doped for transforming spin-frustrated semiconductors into ferromagnets [5-7]. However, these transition metals with local magnetic moments have some limitations when acting as the doping elements because magnetic secondary clusters have been found to be ferromagnetic [8-10].

In this study, we investigated Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires. In the previous study, we investigated Cu-doped GaN nanowires and found evidence of ferromagnetism [11]. Cu is a non-magnetic element; however, if it is doped into a semiconductor in such a way that it is in a divalent state, the partially filled d states of the Cu^{+2} ions render it a candidate for ferromagnetism [11]. Meanwhile, the $\text{In}_x\text{Ga}_{1-x}\text{N}$ compound semiconductor has the accessibility of band gap modulation, which carries a high potential for wide-ranging applications. If magnetism is observed in Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires, it is the first observation of evolution of magnetism in In-Ga-N semiconductor system by doping of a non-magnetic element. It suggests band gap tunable, magnetic In-Ga-N semiconductors that could be versatile DMSs toward spintronics.

* Correspondence: hjc@yonsei.ac.kr

¹Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Republic of Korea

Full list of author information is available at the end of the article

Methods

Single $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires were synthesized using Ni/Au bi-metal catalysts deposited on sapphire ($\text{c-Al}_2\text{O}_3$) substrates in a horizontal hot-wall chemical vapor transport system. The thicknesses of the Ni and Au were 0.5 and 2 nm, respectively. Between the bi-metal catalysts and the sapphire substrates, a 30-nm single-crystalline GaN film was inserted to reduce lattice mismatch. Trimethylgallium (TMGa), trimethylindium (TMIn), and ammonia flowed as precursor gases, thereby supplying the sources of indium and gallium. CuCl powder (purity 99.99%) was inserted into the center of a quartz tube at intervals of 2 in. The substrates were loaded into a reactor and heated to the growth temperature of 700°C under flows of 100 sccm H_2 and 100 sccm N_2 . The TMGa, TMIn, and NH_3 were then allowed to flow for 10 min. Some nanowires were annealed at 800°C by using a rapid thermal annealing process. The composition of $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires could be modulated with the range $0 \leq x \leq 0.51$ that the band gap energies correspond from 2.17 to 3.1 eV by adjusting the amount of TMGa and TMIn and the growth temperatures. Among these, the $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires with $x = 0.09$ that corresponds to the band gap energy of 3.1 eV were chosen for this experiment. The concentration of Cu in these nanowires was analyzed as 1.8%.

The nanowires were characterized using transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS). The magnetic properties of the nanowires on the substrate were measured in a superconducting quantum interference device (SQUID) magnetometer, with corrections being made to take into account the diamagnetic contribution from the substrate. Anomalous X-ray scattering (AXS) and X-ray magnetic circular dichroism (XMCD) measurements were carried out at the 2A beam-line of the Pohang Light Source (PLS). For the XMCD measurement, the degree of circular polarization of the incident light was set to be 95%, and a 0.5-T magnetic field that is produced by an electromagnet was applied along the surface normal to the sample to align the spin moment.

For electric measurement, the nanowires were sonicated in ethanol and dispersed to $\text{SiO}_2/\text{p-doped Si}$ substrate. We deposited a Ti/Au electrode of 70 nm on one $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowire channel using conventional photo-lithography and a sputtering system. A 300-nm SiO_2 oxide layer and a highly p-doped Si layer were used for the bottom gate insulator and gate electrode, respectively.

Results and discussion

Figure 1a shows a scanning electron microscopy (SEM) image of the Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires grown on the substrate with Au/Ni as bi-catalyst [12]. The nanowires have diameters in the range of 80 to 150 nm and lengths in the range of hundreds of micrometers. The

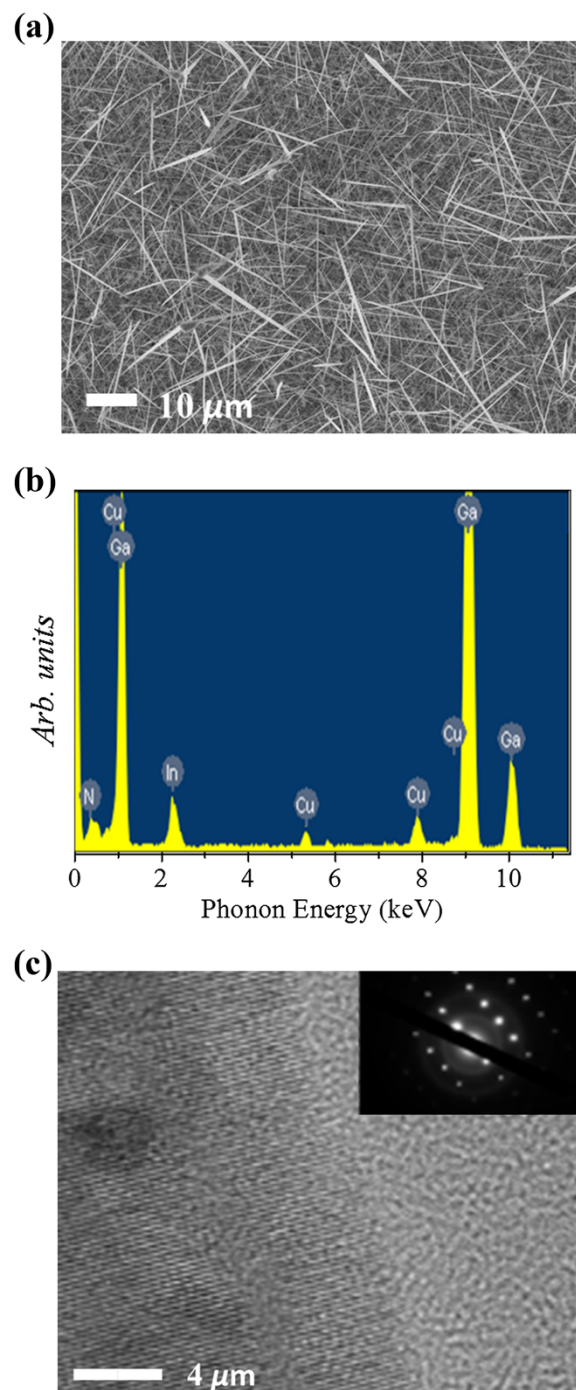


Figure 1 SEM, EDS, and HRTEM images and SAED pattern of nanowires. (a) Typical SEM image of Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires. (b) EDS image of the nanowire. (c) HRTEM image and the SAED pattern (inset) of an 80-nm-diameter nanowire.

nanowires were sonicated in ethanol and dropped to molybdenum grids for the EDS and TEM analyses. EDS was used to determine the composition of Cu in the Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires. Figure 1b shows the respective Cu concentrations at the center of the Cu-doped

$\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowire. The average Cu concentration was about 1.8%. Figure 1c shows a high-resolution TEM image, which illustrates that the nanowires are single crystals without defects and secondary phases. In the inset of Figure 1c, the selected area electron diffraction (SAED) pattern shows the nanowires grown along the [001] direction. We also characterized the annealed nanowires and found any structural and compositional changes in the nanowires.

Figure 2 shows the field dependence of magnetization for Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires, which was measured with a SQUID magnetometer at room temperature and after rapid thermal annealing (800°C). The inset of Figure 2 shows the magnetic properties of the as-grown $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires, which indicate diamagnetism at room temperature. This is due to the fact that Cu may be interstitially doped into $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires, since this type of doping is more energetically favorable than substitution doping [13-15]. In order to resolve this issue, the Cu dopants in the $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires were activated through rapid thermal annealing under a flow of N_2 gas. It is known that annealing dissociates Cu by occupying the interstitial sites and substituted Ga or In vacancies in the InGaN lattice. This leads to an increase in the hole concentration, which is essential for the evolution of ferromagnetism in the doped semiconductors [16-18]. As expected, we observed the clear hysteresis loops after rapid thermal annealing (800°C) even at room temperature, which indicates that nanowires possess ferromagnetism with a Curie point exceeding room temperature [18]. The magnetization increases steeply at a low magnetic field and saturates at about >0.15 T. The magnetization for Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires in Figure 2 is shown to be $0.8 \mu_B$ ($1 \mu_B \times 10^{-24} \text{ Am}^2$) per Cu atom at room temperature.

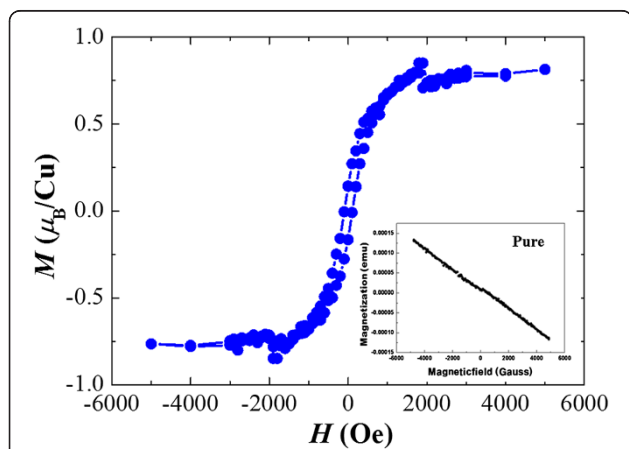


Figure 2 Magnetic properties after rapid thermal annealing under a flow of N_2 . The inset shows the magnetic properties of pure $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires, indicating diamagnetism.

To investigate whether Cu dopants are incorporated in the crystalline lattice of $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires or not, we measured AXS for the $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires around the Cu K absorption edge. Figure 3a shows the L -edge absorption spectra for Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires. The absorption spectrum peaks are separated into two regions of L_3 and L_2 , due to the spin-orbit split of the core levels. This is consistent with the well-known 930- to 931-eV peak of CuO corresponding to the $3d^9$ ground state ($2p$ to $3d$ dipole transition) [11]. The Cu absorption spectrum peak and the largest peak for Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires are located at the same energy of 930 eV for the $3d^9$ ground state of CuO. There is also another identical but smaller peak at an energy level that is 3.5 eV higher. There

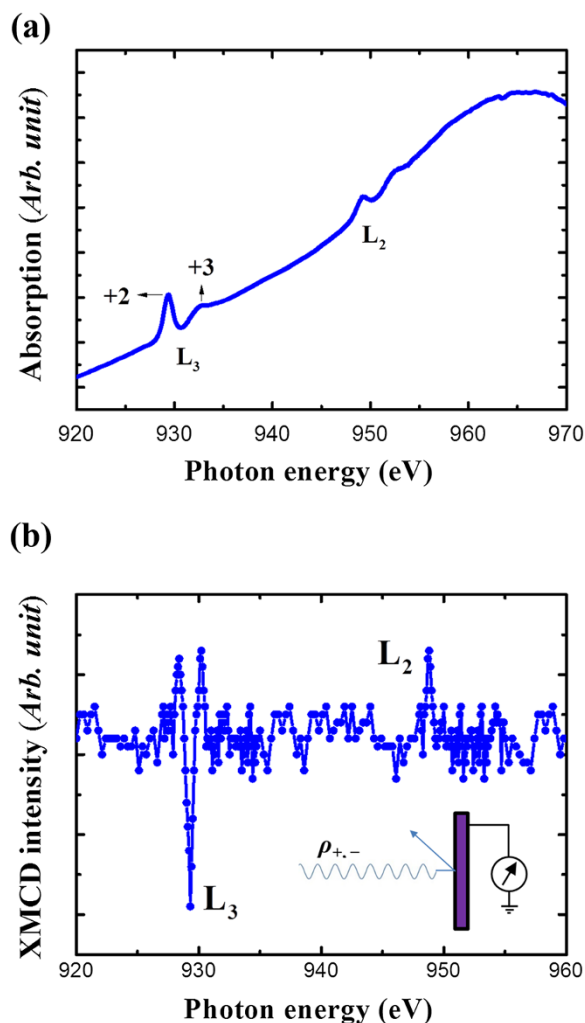


Figure 3 AXS spectra at the Cu $L_{2,3}$ -edge and XMCD data. (a) AXS spectra at the Cu $L_{2,3}$ -edge for Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ measured at 300 K. The inset shows the AXS spectra at the Cu $L_{2,3}$ -edge for reference CuO powder. (b) XMCD data showing the difference between the Cu $L_{2,3}$ -edge AXS spectra for the different spin directions (ρ_+ and ρ_-) of nanowires measured at 300 K.

is no such corresponding peak in divalent (2+) or monovalent (1+) Cu compounds [19,20]. It is common in the AXS spectra that higher valence states of 3d transition metals appear at energies that are higher by 2 to 4 eV because of the decreased Coulomb energy between the core hole and valence electrons of the final state [21-23]. Accordingly, we expected that it is related to the trivalent (3+) state. The identical line structure is reproduced at the L_2 region [19,20]. It is thus confirmed that the electronic configuration of doped Cu is mainly $3d^9$. The formal ionic valence of Cu at cation sites is trivalent; however, it seems that the locally divalent state is preferred for covalent bonding with nitrogen. This suggests that the ionocovalent bonding nature of the Cu 3d orbital with the surrounding semiconductor medium provides the Cu atom with a mixed electron configuration.

If such a case occurs, then the spins of the 3d orbital are not paired and the doped Cu should have a local spin magnetic moment. To check whether the local spin moments align ferromagnetically or not, the XMCD spectra of Cu $L_{2,3}$ absorption edges were also measured. As shown in Figure 3b, the dichroism signal was measured successfully. The theoretical multiplet spectrum for the $3d^9$ configuration in a wurtzite crystal field is reproduced. Consequently, it is proven that the doped Cu provides a local magnetic moment, and this is the cause for the ferromagnetism of the Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires at room temperature. In this system, no XMCD dichroism signal at the Ni $L_{2,3}$ -edge in the samples was observed, such as in the metallic or secondary phase of the Ni catalyst employed in the growth of the nanowire. This further suggests that the nanowires are ferromagnetic at room temperature and that the induced host moments are clearly associated with the ferromagnetic phase in the Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$. This also provides compelling evidence against any role in the origin of ferromagnetism of the secondary phase and impurity.

We observed the Cu 3d state and its four nearest neighboring N 2p states to understand the mechanism that stabilizes the ferromagnetic state in the Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowire system [24]. In the majority spin channel, the Cu 3d overlaps with the four nearest neighboring N 2p states at the CuN_4 tetrahedron with reduced magnetization; additionally, in this channel, the 2p state of the four connecting N atoms contributes significantly to the unoccupied states. These characteristics indicate strong hybridization between Cu and its four neighboring N atoms. This strong hybridization induces finite magnetization of the Cu atom as well as the neighboring N atoms. The induced magnetic moments generated by the delocalized Cu ion indicate that a long-range p - d exchange interaction can occur in the Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowire system. Indeed, recent theoretical studies have shown that this system is a promising DMS

possessing ferromagnetism, which can be explained in terms of the p - d hybridization mechanism, with a Curie temperature around 350 K.

The annealing could make the nanowires increase the hole concentration due to dissociating Cu by occupying the interstitial sites and substituted Ga or In vacancies in the InGa_N lattice. For investigating the electric properties, we fabricated a field-effect transistor using bottom gate voltage on one Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowire channel after the annealing process, as shown in Figure 4a. In the inset of Figure 4a, the close-up of the triangle nanowire channel and the diameter is about 120 nm, and the channel length is about 1.5 μm . Figure 4 shows the gate voltage dependence of the source-drain current (I_{SD}) at various source-drain voltages (V_{SD}), which indicates n-type behavior. This result is similar to those found in previous papers that reported n-type electrical behavior [11,18], but these are inconsistent with the evolution of hole-mediated

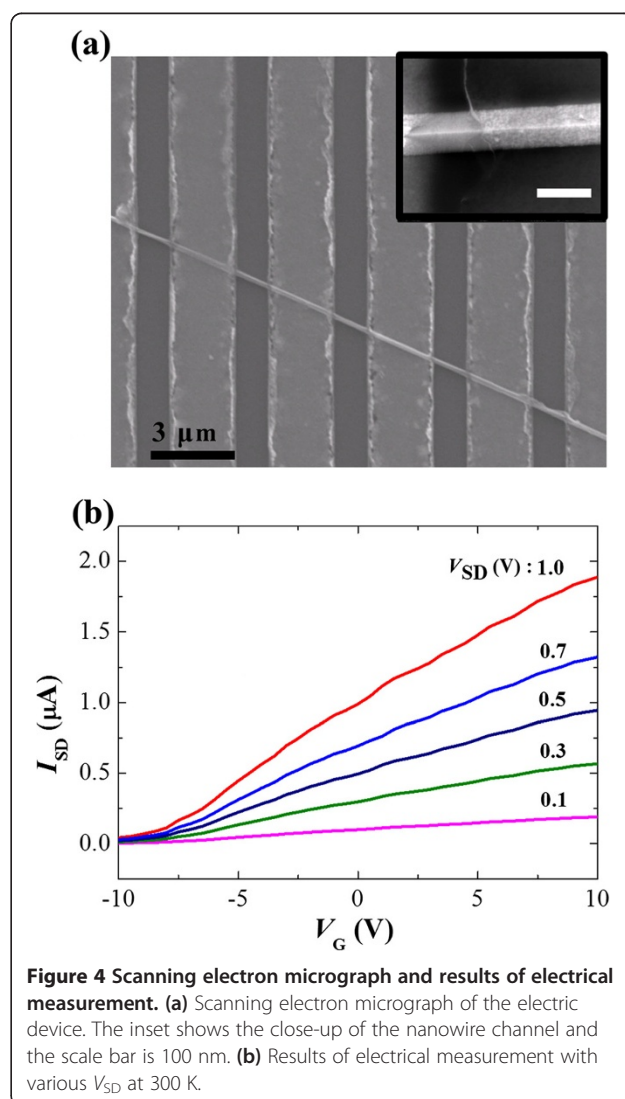


Figure 4 Scanning electron micrograph and results of electrical measurement. **(a)** Scanning electron micrograph of the electric device. The inset shows the close-up of the nanowire channel and the scale bar is 100 nm. **(b)** Results of electrical measurement with various V_{SD} at 300 K.

magnetism. The $\text{In}_x\text{Ga}_{1-x}\text{N}$ system including nanowires in this study has n-type electrical behavior due to the structural defects. In the system, Cu could act as p-type dopant if it fully substitutes Ga or In sites and ionized. In this study, however, the Cu dopants may not yet fully occupy the Ga or In sites in the In-Ga-N lattice by the annealing process, and thus, the n-type behavior was still observed although the magnetism was evolved by Cu.

Conclusions

Single-crystal and homogeneous Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires were fabricated and were shown to exhibit ferromagnetism at room temperature after rapid thermal annealing (800°C) under a flow of N_2 gas. XMCD spectra of Cu $L_{2,3}$ absorption edges were measured, and the dichroism signal was calculated successfully. It is proved that the doped Cu provides the local magnetic moment and is the origin of the ferromagnetism of the Cu-doped $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires at room temperature. It is the first observation of the evolution of magnetism in In-Ga-N semiconductors by doping of a non-magnetic element. By considering the band gap tunable, direct band gap nature of In-Ga-N systems, such an evolution of magnetism suggests versatile DMSs toward spintronics.

Abbreviations

AXS: anomalous X-ray scattering; DMS: diluted magnetic semiconductor; EDS: energy-dispersive spectroscopy; PLS: Pohang Light Source; SEM: scanning electron microscopy; SQUID: superconducting quantum interference device; TEM: transmission electron microscopy; XMCD: X-ray magnetic circular dichroism.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

YHP carried out the main part of the structural analysis and drafted the manuscript. RH participated in the synthesis and structural analysis. SWK and DS participated in the discussion of the cross-sectional TEM sampling and EDS. RH and YHP analyzed the AXS and XMCD measurement. T-EP and DS carried out the electric measurement. H-JC participated in the design of the study, draft preparation, and coordination. All authors read and approved the final manuscript.

Acknowledgements

This work was supported by a grant (NRF-2012R1A2A1A03010558) from the National Research Foundation (NRF) of Korea funded by the Ministry of Science, ICF, and Future Planning (MSIP), Korea, and by the Agency for Defense Development (ADD) of the Republic of Korea.

Author details

¹Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Republic of Korea. ²Spin Convergence Research Center, Korea Institute of Science and Technology (KIST), Seoul 136-791, Republic of Korea.

Received: 4 November 2014 Accepted: 11 December 2014

Published: 7 January 2015

References

- Heedt S, Morgan C, Weis K, Bürgler DE, Calarco R, Hardtdegen H, et al. Electrical spin injection into InN semiconductor nanowires. *Nano Lett.* 2012;12:4437.

- Zhang S, Dayeh SA, Yan L, Crooker SA, Smith DL, Picraux ST. Electrical spin injection and detection in silicon nanowires through oxide tunnel. *Nano Lett.* 2013;13:430.
- Kum H, Heo J, Jahangir S, Banerjee A, Guo W, Bhattacharya P. Room temperature single GaN nanowire spin valves with FeCo/MgO tunnel contacts. *Appl Phys Lett.* 2012;100:182407.
- Ohno H. Making nonmagnetic semiconductors ferromagnetic. *Science.* 1998;281:951.
- Lee JS, Lim JD, Khim ZG, Park YD, Pearson SJ, Chu SNG. Magnetic and structural properties of Co, Cr, V ion-implanted GaN. *J Appl Phys.* 2003;93:4512.
- Neal JR, Behan JA, Ibrahim RM, Blythe HJ, Ziese M, Fox AM, et al. Room-temperature magneto-optics of ferromagnetic transition-metal-doped ZnO thin films. *Phys Rev Lett.* 2006;96:197208.
- Matsumoto Y, Murakami M, Shono T, Hasegawa T, Fukumura T, Kawasaki M, et al. Room-temperature ferromagnetism in transparent transition metal-doped titanium dioxide. *Science.* 2001;291:854.
- Zaja M, Gosk J, Granka E, Kaminska M, Twardowski A, Strojek B, et al. Possible origin of ferromagnetism in (Ga, Mn)N. *J Appl Phys.* 2003;93:4715.
- Kim JY, Park JH, Park BG, Noh HJ, Oh SJ, Yang JS, et al. Ferromagnetism induced by clustered Co in co-doped anatase TiO_2 thin films. *Phys Rev Lett.* 2003;90:017401.
- Ando K, Saito H, Jin Z, Fukumura T, Kawasaki M, Matsumoto Y, et al. Magneto-optical properties of ZnO-based diluted magnetic semiconductors. *J Appl Phys.* 2001;89:7284.
- Seong HK, Kim JY, Kim JJ, Lee SC, Kim SR, Kim U, et al. Room-temperature ferromagnetism in Cu doped GaN nanowires. *Nano Lett.* 2007;7:3366.
- Ha R, Park E, Park TE, Kim SW, Choi HJ. Vertical growth of GaN nanowires using Cu based multi-catalyst. *Int J Nanotech.* 2013;10:828.
- Schuber R, Ganz PR, Wilhelm F, Rogalev A, Schaadt DM. Local electronic structure of Cu-doped GaN investigated by XANES and x-ray linear dichroism. *Phys Rev B: Condens Matter Mater Phys.* 2001;64:155206.
- Elsayed M, Rehberg RK, Moutanabbir O, Anwand W, Richter S, Hagendorf C. Cu diffusion-induced vacancy-like defects in freestanding GaN. *New J Phys.* 2011;13:013029.
- Rosa AL, Ahuja R. Weak ferromagnetism in Cu-doped GaN. *Appl Phys Lett.* 2007;91:232109.
- Lin YJ. Excimer-laser-induced activation of Mg-doped GaN layers. *Appl Phys Lett.* 2004;84:2760.
- Moon YT, Kim DJ, Park JS, Oh JT, Lee JM, Park SJ. Recovery of dry-etch-induced surface damage on Mg-doped GaN by NH_3 ambient thermal annealing. *J Vac Sci Technol, B: Microelectron Nanometer Struct Process Meas Phenom.* 2004;22(2):489.
- Lee CM, Lim JM. Effects of the annealing temperature on the electrical properties of p-type ZnO films grown on (0001) sapphire substrates by using atomic layer epitaxy. *J Korean Phys Soc.* 2006;49(3):913.
- Van der Laan G, Patrick RAD, Henderson CMB, Vaughan DJ. Oxidation state variations in copper minerals studied with Cu 2p X-ray absorption spectroscopy. *J Phys Chem Solids.* 1992;53:1185.
- Giori M, van Acker JF, Czyzyk MT, Fuggle JC. Unoccupied electronic structure and core-hole effects in the x-ray-absorption spectra of Cu_2O . *Phys Rev B.* 1992;45:3309.
- Scarpulla MA, Cardozo BL, Farshchi R, Hlaing Oo WM, McCluskey MD, Yu KM, et al. Ferromagnetism in $\text{Ga}_{1-x}\text{Mn}_x\text{P}$: evidence for inter-Mn exchange mediated by localized holes within a detached impurity band. *Phys Rev Lett.* 2005;95:207204.
- Sasaki T, Sonoda S, Yamamoto Y, Suga K, Shimizu S, Hori H. Magnetic and transport characteristics on high Curie temperature ferromagnet of Mn-doped GaN. *J Appl Phys.* 2002;91:7911.
- Chaboy J, Munoz-Paez A, Carrera F, Merklings P, Marcos ES. Ab initio x-ray absorption study of copper K-edge XANES spectra in Cu(II) compounds. *Phys Rev B.* 2005;71:134208.
- Lew K, Redwing JM. Growth characteristics of silicon nanowires synthesized by vapor-liquid-solid growth in nanoporous alumina templates. *J Cryst Growth.* 2003;254:14.

doi:10.1186/1556-276X-10-3

Cite this article as: Park et al.: Magnetic $\text{In}_x\text{Ga}_{1-x}\text{N}$ nanowires at room temperature using Cu dopant and annealing. *Nanoscale Research Letters* 2015 **10**:3.